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February 18, 2009

Dr. Doug Kirkpatrick Program Manager Defense Advanced Research Projects Agency 3701 North Fairfax Drive Arlington, VA 22203-1714

Dear Dr. Kirkpatrick:

Subject: Fuel Qualification Plan Deliverable; No-Crack Pathway to Renewable Domestic JP-8 (RDJP-8); Contract No. W911NF-07-C-0046; EERC Funds 9534, 9535, 9536, 9537, 9538, 9539, 9540, and 9541

Enclosed please find the subject deliverable fuel qualification plan entitled "Commercial Approval Plan for Synthetic Jet Fuel from Hydrotreated Fats and Oils," produced by the subcontractor, Southwest Research Institute, under the subject contract.

Thank you for your support of this project. If you have any comments or questions regarding the enclosed fuel qualification plan, feel free to contact me by phone at (701) 777-2982 or by e-mail at taulich@undeerc.org.

Sincerely, Walnut

Ted R. Aulich

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COMMERCIAL APPROVAL PLAN FOR SYNTHETIC JET FUEL FROM HYDROTREATED FATS AND OILS

Fuel Qualification Plan

(for the period of March 26, 2007, through April 24, 2009)

Prepared for:

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COMMERCIAL APPROVAL PLAN FOR SYNTHETIC JET FUEL FROM HYDROTREATED FATS AND OILS

This document provides a guide for working through the commercial approval process for qualifying jet fuel containing materials from hydrotreated fats and oils (HRJ for Hydrotreated Renewable for Jet). It is purposefully simple to keep focus on the task at hand, which could easily be obscured in the analysis details. The guide is divided into three sections.

- 1. The Immediate Plan the items than need to be done next
- 2. The Program Outline An outline of the overall effort to be undertaken to go from blend stock synthetic paraffinic kerosine (SPK) to fully synthetic jet fuel (FSJF)
- 3. The Aromatics Effort A discussion of the specific activities that will be needed to go beyond the approval of HRJ SPK.

Before proceeding a note about the role of the original equipment manufacturers (OEMs). Throughout the effort to put synthetic jet fuel in the field the acceptance of the OEMs has been critical to the process, for both military and commercial interests. This is because they are the arbiters of Flight Safety. This is both a contractual (DOD) and regulatory (FAA) imperative.

The Immediate Plan

The initial response of the OEMs to idea of making jet fuel from organic oils was to recommend following the complete draft Practice for Approval of Turbine Fuels and Additives. This was driven by their experience, some of it very negative, with the other more well known organic oil derived fuel, BioDiesel. BioDiesel is methyl ester of the fatty acid (FAME) that comes from the triglycerides that compose the organic oil. The HRJ SPKs are deoxygenated materials that are processed in a manner similar to common FT schemes.

Since the HRJ materials are so similar in nature to Fischer Tropsch (FT) type materials that were nearly through the process the idea of starting at the most basic level seemed unreasonable. Through the exchange of significant data, in public and private, the OEMs have agreed, in principle, that the HRJ derived SPK should be evaluated in the same fashion as FT SPK. While still a large task, it is significantly smaller than what could be required from a process without an existing analog.

The goal for the immediate future will be the development of a research report for HRJ SPK. In final form it should be similar to the research report for FT SPK that has just been submitted for ASTM ballot. The process can be outlined, on a per candidate HRJ SPL basis, as follows:

1. Conduct the Combined Specification (Table 1: ASTM D1655 and Table 2: MIL-DTL-83133F), see Table 1 on the neat HRJ SPK

- a. This will illustrate that the basic properties are similar to those of FT SPK. These properties, except for distillation that is understood to be different, are critical to proceeding.
- b. Compare to expected values for FT SPK
- c. Review this data with OEM representatives, if necessary. This would be needed if there were data at variance from the FT experience but not, in itself, a reason to reject this material.
- 2. Conduct the complete Fit for Purpose (FFP) testing series, listed in Table 2, for the neat HRJ SPK.
 - a. This data will be compared to the same data generated for the FT SPKs.
 - b. This data will need to be reviewed by the OEMs. This is a mandatory step.
- 3. Prepare blends of the HRJ SPK with jet fuel and then complete the combined specification analyses (see Table 1) for the neat jet fuel and the blend.
 - a. Experience with FT SPK leads to an expectation, by the OEMs, of how the blending will affect jet fuel and the same will be evaluated for HRJ SPK
 - b. Review with OEM representatives.
- 4. Conduct the FFP matrix and the equivalent procedures analysis, as indicated in Tables 2 and 3, for neat jet fuel and the blend.
 - a. This will be used to confirm that the blends are reasonable statistical representations of what is expected for jet fuel.
 - b. Review with OEM representatives.
 - c. Coordinate this information into a joint research report.
- 5. Based on the data generated for the research report and the OEM/FAA/DOD review the specification groups can move to add HRJ SPK.
 - a. If HRJ is found completely equivalent:
 - i. DOD could modify MIL-PRF-83133F to include it directly.
 - ii. ASTM could modify the new DXXXX specification by adding the research report.
 - b. If a small amount of additional analysis is needed:

- i. The respective SPK conformance tables and test requirements could be modified.
- c. If there are significant differences:
 - i. New Appendix for MIL-PRF-83133
 - ii. New Annex for DXXXX

Originally there was discussion of significant engine/component testing, similar to that done on the FT SPK, but as more data was presented that showed the HRJ SPK was very similar to FT SPK that imperative has diminished. While there may still need to be some engine/component testing the more closely the HRJ material can be associated with the FT the less testing will be required. Right now the OEMs are being very circumspect about any engine/component testing that will be needed. This is due to both the conservative nature of the business and the preliminary nature of the data available for their analysis. As more data is generated that shows that HRJ SPK is essentially identical to FT SPK it will be possible to narrow the component testing requirements. It will be incumbents upon the HRJ producers to ask for clarification about what perceived difference from FT SPK that would drive a need to re-do tests that had been previously conducted.

Even a little comparative data analysis has resulted in a more favorable disposition to the goal. For instance, an initial comparison of the iso:norm ratios and molecular weight (MW) distribution in the initial version of this report (previously provided) and for selected HRJ SPKs showed the latter to be within the existing experience and the addition of three more FT SPKs did not change that. While this provides more confidence the HRJ derived materials will be essentially the same as the FT materials the complete FFP analysis is needed for confirmation.

In the FT SPK research report there is analysis of five (5) FT SPKs and the blends thereof. The OEMs will expect a similar level of effort for the HRJ SPK analysis. The FT SPK report covers a variety of Fischer-Tropsch processes and conditions. The HRJ SPK analysis should also represent a variety but with an emphasis on feedstock. The variation should be on both fatty acid size and origin. A good cross section would be algae, three (3) vegetable oil with a range of fatty acid MWs (example: coconut, soy, canola) and yellow grease derived HRJ SPKs. With the number of entities currently pursuing this goal, no single group should have to deliver more than one complete analysis program.

The pattern that took an extended time to generate for the FT SPK is now set so the basic items are in place. It now rests on the execution. One thing that would be a major improvement over the FT SPK effort would be better coordination. This would be enhanced by working with a coordinating group to ensure timely development of the requisite data. This could be the existing ASTM Task Force on Hydrotreated Renewable Jet Fuel, a more proactive effort, such as a combine, of the concerned parties or a combination of both. The US Air Force provided the funding for some of the testing and the production of the final coordinated FT SPK report. While there are indications they will provide input from their HRJ SPK program, it does not appear that

they will fund the HRJ SPK effort. SwRI has experience in both organizing test and evaluation combines and organizing fuel qualification reports so this would be an appropriate further task.

The ASTM Aviation Fuel Subcommittee is moving to ballot the following:

- 1. Clarifying language for D1655 on how fuel components from alternate sources are and will be controlled.
- 2. The Research Report on FT SPKs and blends thereof.
- 3. Proposed Specification DXXXX for Aviation Turbine Fuels with Synthetic Components.

Basically the proposed language for D 1655, Standard Specification for Aviation Turbine Fuels, notes the fact that the concept of synthetic hydrocarbons has been agreed to. Further it states that, currently, fuels containing synthetic hydrocarbons need to conform to the existing fuel composition and that formulation guidance will be found in a new specification (ne: DXXXX). This was a major victory in achieving a workable solution for the introduction of alternative synthetic fuel sources into the jet fuel pool. A significant portion of the aviation fuel community wanted to modify D1655 directly to recognize the use of FT SPK blend components. An initial effort to do so resulted in supportable negative ballots that the proposed changes had both too much and too little information. The basic fact is that D1655 is an article of commerce not a formulary. It describes the common nature of all jet fuel. It cannot accommodate specialty fuels. While it is technically possible that the change could be made the difficulties and effort required would have resulted in a very unfavorable climate for the introduction HRJ SPK.

The approval of the research report for FT SPK will be a benchmark for hydrocarbon component for jet fuel analyses. ASTM is very precedent driven and HRJ SPK materials would have to demonstrate significant deviations from FT SPK or new information would have to be found to require significant deviation from the same formula.

The proposed specification, DXXXX, has major issues to be resolved before approval in final form and balloting it is a way to move to resolving those issues. Of particular note are the needs to find adequate ways to describe the fuel chemistry and ensure an adequate distillation range.

The industry understands that the output of an FT SPK plant, as well as coming to understand the same for HRJ SPK, is essentially paraffinic hydrocarbons. There is gap between essentially and solely paraffinic hydrocarbons with which the industry must deal. There is some evidence that the FT SPK programs produce some minor amount of aromatics (and one would assume the very similar on the back-end HRJ SPK processes would too). Right now there is no known suitable standard test for such low level aromatics. SwRI is working on a modification of the existing D2425, Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry, using only the non-polar portion of the test.

The current understanding of suitability is with SPKs that cover a range (usually 4 or more) of carbon numbers in the jet fuel range. The question is how to specify this adequately. To date the approach has been to specify distillation characteristics for the SPK and the final fuel but that

approach my not be the best solution. One alternative would be a GC based carbon number range analysis. For instance using the already allowed simulated distillation method, D2887, and simply count the main peaks on the resultant output graph. While simple in concept both of these approaches need codification.

The result of this activity is that while the HRJ SPK is well behind FT SPK in data and analysis there is time to catch up. All of the things that are in question for the specification are issues for both types of SPK. The HRJ SPK group needs to work diligently to:

- 1. Get the appropriate research report together in a timely manner, preferably before the new specification is issued.
- 2. Participate with the generation of the specification language to ensure that it is not accidentally limiting.

DXXXX is designed to be a modular approach to the addition of non-petroleum synthetic hydrocarbons to jet fuel. This modularity is controlled by annexes, mandatory information in ASTM standards. The initial annex for Hydrotreated Synthetic Paraffinic Kerosines should be sufficient to cover both the FT and HRJ varieties, needing only the appropriate approved research reports. If testing proves the HRJ SPKs need additional controls beyond those important for FT SPK this could be handled by as little as including a new classification and test requirements for the HRJ SPK to as much as adding a new annex. It will not require a new specification or further modification to D1655.

The Program Outline

The information in the previous section "The Immediate Plan" covers part one below. It assumes there is not significant difference between HRJ SPK and FT SPK, a position supported by the bulk of the data so far. Moving forward with FSJF blends as blend stocks and then as stand alone fuel technically retreads the same course of generating supporting data and seeking approval. There are, however, structural issues of what actually needs to be in jet that have to be resolved before proceeding with FSJF. Those issues will be discussed in the last section.

- 1. Approval of HRJ SPK as a Blend Stock
- 2. Approval of HRJ FSJF as a Blend Stock
 - a. The primary issue to be dealt with is the source and nature of the aromatics and cycloparaffins:
 - i. Potential synthesis routes for aromatics and cycloparaffins bring new issues that have not been examined during the SPK effort.
 - (1) Recent work (reported at the MACCR [Multi Agency Coordinating Committee on Combustion Research] meeting) has shown a direct structural interaction with combustion properties.

- (2) Catalytic processes often result in very specific types of structures not the random selection typical from crude petroleum.
- ii. History suggests that these materials are where the majority of thermal stability issues are found.
- iii. The SASOL aromatics are from unique decades old processes so their use is informative but not conclusive.
- b. Once the industry feels the use of synthetic aromatics is appropriate, using FSJF as a blend stock provides a conservative approach to introducing the new material to commerce.
- c. The process will then follow the same path as that for HRJ SPK
- 3. Approval of HRJ FSJF as Stand Alone Fuel
 - a. The issues once again concern aromatics and cycloparaffins but this time the issue will be need and requirement for each
 - i. How much aromatics are needed if needed at all?
 - (1) Elastomer compatibility is cited as the primary need
 - ii. How much cycloparaffin is needed?
 - (1) Does it have a significant impact on altitude relight?
 - iii. Do we need both?
 - (1) If so how much?
 - (2) Is density really an overriding operational necessity?
 - b. Once these questions are answered we can move forward to a FSJF and use the same path as before:
 - i. There is a possibility that they will not be needed at all because of:
 - (1) Better emissions
 - (2) Superior thermal stability

The Aromatics Effort

The need for aromatics, and to some extent cycloparaffins, is the big question at play for the future of synthetic aviation turbine fuels. While there is no minimum requirement typical jet fuel has more than 14% aromatics. There are lower values reported but they are rare. Such aromatic content is needed to achieve the minimum required density. There is also an issue of elastomer compatibility for certain legacy aircraft. On the negative side aromatics are a known sources of thermal stability and emissions problems, plus there is new data that indicates the specific chemical structure of aromatics can have negative impacts of fuel combustion characteristics. The requisite balance is in question.

While there is a broad consensus that understanding the need for aromatics is an important step in moving forward on the approval of a FSJF little real progress has been made. According to the OEMs, they are awaiting the results of an in depth study on aromatics being conducted by AFRL. Although the details are vague this study is supposed to consider the need for and the problems with aromatics in the fuel.

If there is to be a FSJF and aromatics are required then there will have to be a synthetic aromatic source. There is new and growing experience with the use of synthetic aromatics in South Africa. SASOL generates synthetic aromatics for their recently approved FSJF but their process yields an aromatics distribution very similar what can be found in petroleum-derived fuel. Aromatics generated by other processes might not have such variation.

This lack of variation could be a significant problem as it comes back to the desire not to blend jet fuel from single chemical components. New data shows that the basic chemical structure of the aromatics can promote or hinder efficient combustion. This poses a related question, is the elastomer compatibility benefit of aromatics a universal attribute or is it structure related also? These issues are in addition to the known issues of soot and emissions associated with aromatics that will make any aromatic approval a challenge.

The Way Forward

The simple facts are synthetic paraffinic kerosines (SPK) are accepted in principle and synthetic aromatics are an unknown quantity. The hydrotreating inherent in the FT and HRJ SPK processes provides a significant protection against harmful materials and is easing their introduction into the fuel supply. As a blend stock the only negative for SPK is a reduction in fuel density, an issue that would affect only the longest flights. There are many social and political benefits to the production of HRJ SPK but of equal import there are the operational benefits of improved emissions and superior thermal stability. Technically the approval of HRJ SPK appears to be primarily a matter of running tests and gathering data. The goal is clear so the task is manageable.

The actual need for aromatics is unresolved. The only specific benefits are density and elastomer compatibility but those are limited in nature. The long duration flights that could push the density limits are rare. Elastomer compatibility is limited to a small group of legacy aircraft, mostly military, as this issue became a known problem during the conversion from JP-4 to JP-8.

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Previous testing showed that the aromatics portion of jet fuel is the source of thermal stability and emissions problems. New data has revealed that specific aromatic structure can impact fuel combustion characteristics. The demand for aromatics in synthetic fuel blends has been to mimic existing fuel and not for the inherent properties of aromatics.

Since the fuel system could adsorb every bit of HRJ SPK that could be produced for the foreseeable future there would seem to be little demand for synthetic aromatics. In fact more than one refiner has remarked that their jet fuel production limitation is not having enough paraffin to go with their aromatics. Initial use of HRJ FSJF would probably be as a blend stock. This would be the most attractive in locations where the available refined product is routinely low in aromatic content and density.

Table 1. Detailed Requirements for Aviation Turbine Fuel

Combined Tests for D1655 and MIL-DTL-83133F

		Т	Tests Required		
Composition		HRJ SPK	Blend	Jet A/A1/JP8	
Saybolt	D156	*	*	*	
TAN	D3242	*	*	*	
Aromatics	D1319	*	*	*	
Sulfur	D4294	*	*	*	
Mercaptan	D3227	*	*	*	
Volatility					
Distillation	D86	*	*	*	
T50-T10					
T90-T10					
Flash	D93	*	*	*	
Density	D4052	*	*	*	
Fluidity					
Freezing Point	D5972	*	*	*	
Viscosity @ -20C	D445	*	*	*	
Combustion					
net Heat of Combustion	D4809	*	*	*	
Hydrogen Content	D3701	*	*	*	
Smoke Point	D1322	*	*	*	
Naphthalene	D1840	*	*	*	
Calculated Cetane	D976	*	*	*	
Corrosion					
Copper Strip	D130	*	*	*	
Thermal Stability ^a					
JFTOT @ 290°C SPK, 275°C Blend	D3241	*	*	*	
Contaminants					
Existent Gum	D381	*	*	*	
MSEP	D3948	*	*	*	
Additives					
FSII	D5006	*	*	*	
Conductivity	D2624	*	*	*	

^aThe FFP requirement includes a JFTOT Breakpoint. These values will be the starting point. When it passes this and all other Table 1 requirements the Breakpoint can be determined. If these do not pass the process will need to be reviewed.

Table 0. Test FFR Test Metric			Total Books I			
Table 2: Test FFP Test Matrix			HRJ SPK	Tests Required Blend	Jet A/A1/JP8	
1) Hydrocarbon Fuel Chemistry			1110 01 10	Dieliu	3317771701 0	
PIANO		02425	*			
Aromatics with sensitivity of 0.1%		05186	*			
2) Trace Materials						
Metals	r	22711	*			
General Panel by ICP Cu by AA		03711 Cu PE506	*			
Semi-Quant Survey		CP/MS	*			
Organic Elements		0.,0				
C:H	D	05291	*			
N	D	04629	*			
S		05453	*			
Acid Number		03242	*			
Carbonyls, alcohols, esters, phenols	EPA 8		*			
	EPA 8		*			
3) Volatility	EPA 8	3270C				
Boiling Point Distribution		D86	*	*	*	
Vapor Pressure, 40-60°C		D5191	*	*	*	
4) Thermal Stability	_	20101				
Breakpoint	С	03241-X.2	*	*	*	
Ellipsometric Analysis			*	*	*	
5) Viscosity						
-40 to 40°C		0445	*	*	*	
6) Lubricity						
CI/LI conc. 0 to 20 mg/l		05001	*	*	*	
7) Specific heat vs T: -40 to 100C	_			*		
0) D	E	1269	*	*	*	
8) Density vs T	-	24052	*	*	*	
15 & 40°C 9) Surface Tension at two temperatures	L	04052				
-10 & 40°C	г	01331A	*	*	*	
10) Bulk modulus		7100174				
10) Daik Modalao	С	6793	*	*	*	
11) Thermal Conductivity vs T:						
2 temperatures, 30 & 100C	D	2717	*	*	*	
12) Long term storage						
Peroxides: 1, 2, 3, 6 weeks at 65C (5 D3703 tests)		03703	*	*	*	
Gums: 16 hours at 100C		05304	*	*	*	
100 hours at 100C						
13) Fuel compatibility	-	3.405.4D	*	*		
14) Additive colubility and compatibility	L	04054B	•	•	î	
14) Additive solubility and compatibility	г	04054B	*	*	*	
15) O-ring tests on nitrile, fluorocarbon(viton), and fluorosil						
Volume swell Div 18		0412	*	*	*	
Tensile strength		0471	*	*	*	
Hardness	D	02240	*	*	*	
16) Electrical Properties						
Dielectric vs density Goodrich ve	ersion of D	0924	*	*	*	
Conductivity and Response to SDA						
SDA mg/l 0-4	D	02624	*	*	*	
Table 3: Alternative Test Methods						
				Taste Poquiros	1	
Blended Fuel Only 1) Freeze Point			HRJ SPK	Tests Required Blend	Jet A/A1/JP8	
Manual	Г	02386	TINUSER	*	JOI A/A I/JFO	
Automatic		05972		*		
1) Specific energy calculations D 3338 & D 4529 vs D 4809		-				
Bomb		04809		*		
Calc #1	С	03338		*		
Calc #2		04529		*		